



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: B01J 27/053, 27/057, 27/14, C07C 2/58, 4/06, C10G 45/62	A1	(11) International Publication Number: WO 97/18892 (43) International Publication Date: 29 May 1997 (29.05.97)
(21) International Application Number: PCT/US96/18436 (22) International Filing Date: 18 November 1996 (18.11.96) (30) Priority Data: 08/559,819 17 November 1995 (17.11.95) US (71) Applicant: HYDROCARBON TECHNOLOGIES, INC. [US/US]; 1501 New York Avenue, Lawrenceville, NJ 08648 (US). (72) Inventors: HU, Jianli; Apartment #78, Princeton Arms, North #1, Cranbury, NJ 08512 (US). PRADHAN, Vivek, R.; Apartment #75, Princeton Arms, North #1, Cranbury, NJ 08512 (US). (74) Agents: JACKSON, David, A. et al.; Klauber & Jackson, 411 Hackensack Avenue, Hackensack, NJ 07601 (US).		(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: SUPPORTED SOLID SUPERACID CATALYSTS AND METHOD FOR MAKING THEM (57) Abstract <p>This invention provides supported solid superacid catalysts composed of anion-modified oxides/oxyhydroxides of Group IV metals such as hafnium (Hf), tin (Sn), titanium (Ti) or zirconium (Zr), precipitated onto a metal oxide support such as alumina, silica or mixtures thereof having initial surface area of 100-500 m²/gm, and is anion modified by addition of molybdate (MoO₄), phosphate (PO₄), selenate (SeO₄), sulfate (SO₄), or tungstate (WO₄). The catalyst further includes an active promoter base metal such as Co, Ni and Pd on a noble metal such as Pt, Rh, and Ru to improve the catalyst stability against deactivation. These supported solid superacid catalysts are prepared by precipitation of hydroxides of Group IV metal onto the support material, followed by the anion-treatment, addition of the stabilizing promoter metal, and calcination at 500-650 °C temperature. Typical supported solid superacid catalysts have a composition of 70-90 wt.% support material, 5-20 wt.% active transition metal oxide, 4-8 wt.% of the anionic group, and 0.05-5 wt.% of the active stabilizing base or noble promoter metal additive. The resulting catalysts have high final surface areas of 100-450 m²/gm, and provide high catalytic activity for various alkylation and hydrocarbon conversion reactions, such as alkylation of refinery gas for producing high-octane gasoline, cracking and hydroisomerization of long chain paraffins, and conversion of waste plastics and low quality oils waxes to produce value-added lubricating oils and chemicals.</p> <div style="text-align: center; margin-top: 200px;"> <p> No { Ni + Pd OR { Pt + Pd </p> </div>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

SUPPORTED SOLID SUPERACID CATALYSTS AND METHOD FOR MAKING THEM

BACKGROUND OF INVENTION

This patent pertains to improved solid superacid catalysts which utilize a high surface area support material and have high catalytic activity. More particularly, it pertains to
5 such supported solid superacid catalysts which are produced by anion-modification of tetravalent transition metal oxides and stabilized by small amounts of a base or noble metal additive, all precipitated onto a particulate substantially inert solid support material having high surface area.

Many industrial chemical and refinery processes employ very strong corrosive mineral
10 acids for catalyzing various chemical reactions such as alkylation, hydrocracking, isomerization and polymerization reactions on various feedstocks at elevated temperature and pressure conditions to make desired value-added products. Specifically, the production of gasoline alkylate component from isobutane and primary C₄ olefins is a widely used petroleum refinery process for improving the octane
15 characteristics of unleaded gasoline. Such alkylate production for gasoline has become increasingly important as a replacement for aromatic and olefin components in gasoline. The catalysts usually used in such alkylation processes have been either anhydrous hydrofluoric acid or sulfuric acid. For example, U.S. Patent No. 4,209,656 to Prescott et al discloses a process for alkylating isoparaffin and olefin hydrocarbons using sulfuric
20 and fluorosulfonic acid catalyst to produce alkylated hydrocarbons. Also, U.S. 5,414,186 to Child et al discloses an isoparaffin-olefin alkylation process using hydrofluoric acid having a sulfone additive. However, because such uses of strong corrosive mineral acids are environmentally hazardous and undesirable, research work has been directed to the development of useful solid phase superacid catalysts as
25 replacements for such strong corrosive liquid mineral acids such as hydrofluoric and sulfuric acids for industrially important chemical reactions. Also, considerable interest has been focused on the development of strong solid superacids in order to replace corrosive aluminum and boron halides as well as liquid mineral acids, normally employed in oligomerization and polymerization reactions.

30 Anion-modified metal oxides having molybdate, sulfate, or tungstate anions deposited on metal oxides such as zirconia (ZrO₂) and titania (TiO₂), have been shown to possess superacidity characteristics. Solid superacid catalysts reported or patented so far apparently have consisted of ZrO₂/SO₄ promoted with a noble metal platinum (Pt) or palladium (Pd), and some publications have reported that other transition metals can be

used as promoters. Also, solid superacid catalyzed reactions reported in the literature have been isomerization of n-butane and alkylation of light paraffin/olefins (C_3 - C_5) which are normally carried out at low temperature and pressure conditions. However, hydrocracking of long-chain hydrocarbons using solid superacid catalysts require
5 hydrogen pressure to stabilize the catalyst. In general, the solid superacids reported so far as catalysts have been associated with some disadvantages such as high cost and rapid deactivation on-stream by coking due to their high intrinsic acidic character.

Certain anion-promoted solid superacids have been found to catalyze reactions of alkylation, isomerization and hydrocracking of hydrocarbons as generally disclosed in the
10 following publications and patents. Hino et al in "Reactions of Butane and Isobutane Catalyzed by Zirconium Oxide Treated with Sulfate Iron", *Journal of the American Chemical Society*, Oct. 10, 1979, pp 3469, disclosed a preparation of ZrO_2/SO_4 catalyst which is active for isomerization of n-butane at room temperature. In *Chemical Week*, Nov. 25, 1987, the treatment of zirconium, titanium and iron oxides with sulfuric acids
15 to produce "sulfated" inorganic oxides that show superior catalytic activity for alkylation of ortho-xylene is disclosed. Baba et al in Japanese Patent, 61-2633932, disclosed that hydrocarbons were isomerized at reaction temperature below 400°C using as catalyst sulfated metal oxides promoted with small amounts of noble metals such as platinum, ruthenium, rhodium, palladium, osmium and iridium. The function of these noble metal
20 promoters are believed to increase the long term performance of solid superacids by hydrogenating strongly absorbed carbon cations which cause coking of solid superacid catalysts. Ebitani et al reported (*Journal of Catalysis*, 130, 257-261, 1991) that the major function of noble metals on solid superacids is to disassociate molecular hydrogen. In Wen et al, "Hydroisomerization and Hydrocracking of n-Heptane and n-
25 Hexadecane on Solid Superacids", *Energy & Fuels*, 1990, 4, 372-379, n-heptane and n-hexadecane were isomerized and hydrocracked on a platinum-doped solid superacid $Pt/ZrO_2/SO_4$ at 130-170°C and 300 psig hydrogen pressure. The bifunctional property of this type of metal-promoted solid superacid is shown to be important in upgrading of paraffins. U.S. Patent No. 4,918,041 to Hollstein et al discloses a solid superacid
30 catalyst comprising ZrO_2/SO_4 modified with small amount of iron and manganese, which has been shown to have enhanced activity for isomerization of n-butane as compared to ZrO_2/SO_4 used alone. U.S. Patent 5,310,868 to Angstadt et al, discloses a process for alkylation of light paraffins and olefins using a solid superacid catalyst having various mixture compositions of metal oxides. European Patent O 653 398 A1 to Angstadt et al
35 disclosed a catalyst containing sulfated zirconia and heteropolyacids for alkylation of paraffins and olefins, and disclosed that the presence of heteropolyacid or

polyoxoanions in the solid superacid catalyst resulted in higher yields of desired high-octane components.

Apparently little information is known regarding cracking of high molecular weight hydrocarbons such as polymers using anion-promoted solid superacid catalysts.

- 5 However, U.S. Patent 4,851,601 to Fukada et al and U.S. 5,079,385 to Wu disclose converting plastic scrap materials into lower molecular weight hydrocarbon products using zeolite type catalysts having acid activity. Also, known organic solid superacids which are essentially polymeric perfluorinated resin sulfonic acids such as Amberlyst™ and Nafion-H™ are commercially available, but are unsuitable for high temperature
10 process operations. Also, other solid superacids include metal fluorides such as antimony fluoride (SbF_5), tantalum fluoride (TaF_5) immobilized on graphite, alumina or silica, but they have serious disadvantages of being corrosive and relatively unstable.

- As disclosed by the above reports and patents, the strong acidity of solid superacids is generated after they are calcined at high temperatures such as above 600°C . However,
15 after such calcination, the known solid superacid catalysts have undesirably limited surface area and catalytic activity, and also have rapid deactivation rates. Thus, the known active solid superacids based upon zirconia compounds have only mediocre and insufficient surface areas needed for providing high catalytic activity, and also require large amounts or concentrations of expensive additive metal compounds. Although
20 some useful solid superacid catalysts have been developed, further improvements are desired to provide highly active solid superacid catalysts having increased surface areas and long active life, and which are useful for various commercially important catalytic reactions.

SUMMARY OF INVENTION

- 25 This invention provides improved supported solid superacid catalysts which have high surface area and high catalytic activity, and which advantageously utilize only small concentrations of active metal compounds. The supported solid superacid catalyst utilizes anion-modification of a tetravalent transition metal oxide of a Group IV metal such as hafnium (Hf), tin (Sn), titanium (Ti), zirconium (Zr), or mixtures thereof,
30 modified by an anion compound such as molybdate (MoO_4), phosphate (PO_4), selenate (SeO_4), sulfate (SO_4) or tungstate (WO_4), and stabilized against deactivation by addition of a suitable active promotor metal, all precipitated uniformly onto a strong particulate support material having high surface area such as alumina (Al_2O_3), silica (SiO_2), or mixtures thereof having an initial surface area of $100\text{--}500\text{ m}^2/\text{gm}$. Suitable active

promotor metals may include small concentrations of a base metal including cobalt (Co), nickel (Ni) or palladium (Pd), or a noble metal including platinum (Pt), rhodium (Rh), ruthenium (Ru) or mixtures thereof. The resulting supported superacid catalyst should have a composition of 70-90 wt. % support material, 5-20 wt. % transition metal oxide, 2-8 wt. % anion modification compound, and 0.05-5 wt. % active promotor metal, and should have final total surface area after calcination of 100-450 m²/g. Preferred supported solid superacid catalyst compositions include either Ni/ZrO₂/SO₄ or Pt/Zr O₂/SO₄ each precipitated onto an alumina (Al₂O₃) support material having 140-45-m²/gm surface area, with the percentage of the support material being 75-85 wt.%, the active transition metal oxide being 6-18 wt. % and the active promotor metal being between 0.1 and 4 wt.% of the total catalyst, which has a final total surface area after calcination of 130-400 m²/gm.

These supported solid superacid catalysts produced according to the invention advantageously utilize significantly lesser amounts of the active metal compounds, but provide high surface area and high catalytic activity along with low deactivation rates, and also have relatively low cost as compared to known liquid or solid superacid catalysts. Because the catalyst active sites are generally proportional to the surface area of the support material being used, the supported solid superacid catalyst of this invention provides substantially increased number of activity sites as compared to the known unsupported solid superacid catalysts. These new supported solid superacid catalysts are effective and useful for alkylation, hydrocracking and isomerization reactions at milder reaction conditions than those required when using conventional corrosive mineral acid catalysts, such as hydrofluoric acid (HF) and sulfuric acid (H₂SO₄).

The supported solid superacid catalysts according to this invention are prepared by precipitation of hydroxides of Group IV metals, such as hafnium, tin, titanium, or zirconium onto a particulate high surface area metal oxide support material such as alumina or silica in a thin uniform layer, followed by anion-treatment with molybdate (MoO₄), phosphate (PO₄), selenate (SeO₄), sulfate (SO₄), or tungstate (WO₄) and also addition of small amounts of a hydrogenation function active promotor metal such as cobalt, nickel, palladium, platinum, rhodium or ruthenium, or mixtures thereof, followed by calcination of the catalyst composition at temperature of 500-650°C for at least 2 hours to produce the final catalyst product. The resulting catalyst having such metals precipitation onto the metal oxide support material can be accomplished from aqueous solutions or by vapor precipitation, which results in the total surface area and the number of active sites for the final catalyst being substantially increased. It has been

found that useful particulate supported solid superacid catalysts of this invention can be advantageously produced which contains a high concentration of 70-90 wt. support material such as alumina or silica; and contain only 5-20 wt. of the active transition metal oxide such as hafnia, stannic oxide, titania or zirconia; 2-8 wt.% of the anionic
5 modification material such as molybdate, phosphate, sulfate or tungstate; and only about 0.05-5 wt. of the stabilizing active base metal such as cobalt, nickel, or palladium, or a noble metal such as platinum, rhodium and ruthenium.

These supported solid superacid catalysts should have an effective particle size of 20-100 mesh (U.S. Sieve Series), equivalent to 0.84-0.15 mm (0.033-0.006 inch), and
10 have a final surface area after calcination of 100-450 m²/gm. The preferred catalyst particle size is 30-60 mesh (0.60-0.25 mm) and has 130-400 m²/gm final surface area. It has been found that these supported solid superacid catalysts provide high catalytic activity reactions with low catalyst deactivation rates, and have relatively low cost for various conversion reactions which are of significant industrial importance. Reactions
15 for which the catalysts of this invention are useful and desirable as compared to known liquid or solid superacids include alkylation of refinery gases for production of high-octane gasoline, cracking and isomerization of long chain paraffins to produce fuel products, conversion of waste plastics and low quality lube oils and waxes to produce value-added lubricating oils and chemicals.

20 This invention advantageously provides improved supported solid superacid type catalysts for which relatively small amounts of the active metal compounds are precipitated onto strong metal oxide support materials having high surface area. The resulting high surface area catalyst provides unexpectedly high catalytic activity, and is useful in various process reactions under relatively mild temperature and pressure
25 conditions. These supported catalysts are environmentally safe and lower in cost than the corrosive liquid acids or unsupported low surface area solid superacids which they replace, and also are capable of periodic regeneration and continued reuse.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a chart showing a correlation of the supported solid superacid catalyst
30 surface area and its activity ration for alkylation for refinery gas feedstreams with a similar unsupported solid superacid catalyst.

FIGURE 2 shows a general comparison of long term performance and deactivation behavior for the supported solid superacid catalysts of this invention with deactivation of known unsupported type solid superacid catalyst.

DETAILED DESCRIPTION

- 5 According to the present invention, it has been unexpectedly discovered that the acidity and catalytic activity of solid superacid catalysts can be at least maintained and usually appreciably improved by precipitating relatively small amounts of active superacid metal compounds uniformly onto a suitable high surface area metal oxide support material such as gamma alumina ($\gamma\text{-Al}_2\text{O}_3$), silica (SiO_2) or mixture thereof. These new and
- 10 improved supported solid superacid catalysts utilize only 5-20 wt.% of anion-modified transition metal oxides known as solid superacids and only 0.5-5 wt. % active promotor metal(s) which are all precipitated uniformly onto the support material such as by aqueous or vapor phase precipitation steps. Suitable metal oxide support materials should have high original surface area of 100-500 m^2/g , and preferably have 140-450
- 15 m^2/g original surface area. The support material effective particle size should usually be between 20-100 mesh (U.S. Sieve Series) (0.84-0.015 mm) and preferably is 30-60 mesh (0.60-0.25 mm). The metal oxide precursors of the supported solid superacid catalyst are introduced onto the support material surface during a hydrolysis step so as to provide a uniform dispersion of the superacid compounds onto the support material.
- 20 The resulting supported solid superacid catalyst which contains only 5-20 wt.% of the active solid superacid materials and exhibit at least comparable and usually appreciably higher catalytic activity in conversion of hydrocarbons as compared to the known unsupported type solid superacid catalysts which contain considerably greater weight percent of the active metals. Instead of using only noble metals (Pt, Pd) as an additive
- 25 hydrogenation function metal, it has been found that less expensive transition metals in Group VIII of the periodic table such as cobalt, nickel and palladium can also be successfully used. The supported catalyst particle strength is adequate to permit use of the catalyst in ebullated or fluidized bed type reactors.
- 30 The enhanced catalytic activity and slow deactivation of the supported solid superacid catalyst according to the present invention makes possible alkylation of light refinery gases to produce the high quality alkylates as gasoline additives for enhancing octane rating of gasoline products, and cracking of high molecular weight hydrocarbons such as plastics, waxes, and low quality lube oils under low severity conditions. By using such supported solid superacid catalysts, cracking of plastics and alkylation of aromatics can

be accomplished in a single reactor at modest temperatures and low pressures to produce alkyaromatic products under low severity conditions. Thus, the present invention provides a series of supported solid superacid catalysts which exhibit high catalytic activity and are more cost effective and attractive for many commercial catalytic process applications than known liquid or solid superacid catalysts. This supported solid superacid catalyst can be used in reactors containing either fixed or fluidized type catalyst beds.

The known solid superacid catalysts usually have an undesirably short useful life such as only 4-6 hours. But the present supported solid superacid catalysts can advantageously maintain high catalytic activity for at least about 72 hours and usually longer before requiring regeneration of the used catalyst. The used supported solid superacid catalysts of this invention can be regenerated by contacting it with air at 500-650°C temperature for 2-4 hours, with the catalyst being retained either in-situ or in a separate container.

Preparation Method for Supported Solid Superacid Catalysts. This invention also includes a method for preparation of the supported solid superacid catalysts having high surface areas. In this method, either alumina or silica support material is used 100 gram of $\gamma\text{-Al}_2\text{O}_3$ having effective particle size of about 60 mesh (U.S. Sieve Series) with initial surface area above 200 m²/g is preheated at 180°C temperature for 24 hours to remove all physically adsorbed moisture. Then, 30 grams of $\text{Zr}(\text{SO}_4)_2$ is slowly added to 300 ml distilled water, the resulting mixture being stirred for 60 min. until the $\text{Zr}(\text{SO}_4)_2$ salt is completely dissolved. The $\gamma\text{-Al}_2\text{O}_3$ particles are then added to the solution with constant stirring, with the stirring speed being increased to maintain the solid $\gamma\text{-Al}_2\text{O}_3$ material in the suspension. Hydrolysis of the prepared solution is carried out by adding 28 wt.% of NH_4OH at rate of 0.7-0.8 ml/min., the hydrolysis step being completed at final pH of 9.5. The particle solution is filtered to remove excess ammonium solution and the supported zirconium hydroxide is washed twice with distilled water, each washing step being followed by a filtration step.

After final washing and filtration, the support particles containing zirconium hydroxide are oven dried at 110°C temperature for 24 hours. Sulfate anion is introduced by sulfating the solid particles with 1.0 N H_2SO_4 for one hour. The sulfated zirconium hydroxide on the alumina support is dried in an oven at 110°C temperature for 12 hours.

- Impregnation of nickel onto the dried catalyst material is carried out by the incipient wetness method. Based on the amount of the sulfated particulate solid used, 0.5-2 wt% nickel is introduced onto the surface of the sulfated solid. Typically, 0.85 grams of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is dissolved in 12 ml distilled water. Impregnation of the solids is completed in three steps; each time 4.0 ml solution containing nickel salt is added to 10.0 grams sulfated solid, followed by drying at 110°C temperature. After introducing all the metal, the resulting sulfated solid is calcined at 620°C temperature for three hours to produce a supported solid superacid catalyst ($\text{Ni}/\text{ZrO}_2/\text{SO}_4/\text{Al}_2\text{O}_3$) having high surface area according to the invention.
- 10 A supported solid superacid catalyst utilizing silica (SiO_2) support material is produced similarly as described above for the alumina support material. The procedure to precipitate solid superacids on SiO_2 support is similar to the preparation of $\text{Pt}/\text{ZrO}_2/\text{SO}_4/\text{AlO}_3$. One hundred grams of SiO_2 gel having surface area of 345 m^2/g is added 800-ml 0.15 M sulfate zirconium solution. Hydrolysis is carried out until final pH of 9.5 is reached. Noble metal platinum additive is introduced the same way as for nickel to provide a supported solid supported catalyst $\text{Pt}/\text{ZrO}_2/\text{SO}_4/\text{SiO}_2$.

- Processes Utilizing Supported Solid Superacid Catalysts.** The supported solid superacid catalysts of this invention can be advantageously used in processes for alkylation of light refinery $\text{C}_3\frac{1}{2}$ C_4 Stream gases to produce gasoline alkylates useful for improving the octane rating of gasoline products. Useful reaction conditions for such a refinery gas alkylation process are 70-250°C temperature, 0-500 psig. pressure, and space velocity of 100-1000 volume gas feed/hr/volume of catalyst bed (Vf/hr/Vc). Preferred process reaction conditions are 100-200°C temperature, 0-200 psig. pressure, and space velocity of 160-400 Vf/hr/Vc .
- 25 These supported solid superacid catalysts can also be advantageously used for cracking high molecular weight polymeric feed materials such as high density polyethylene (HDPE), polyethylene and polystyrene, in a single catalytic reactor to produce aromatic products. Useful reaction conditions for such cracking processes are 100-500°C temperature, and 0-100 psig. pressure. Preferred reaction conditions are 125-450°C, temperature and 10-80 psig. pressure.

This invention will now be described further with the aid of the following examples, which should not be construed as limiting the scope of the invention.

EXAMPLE 1

In order to show a comparison between a typical known unsupported type solid superacid catalyst and a supported solid superacid catalyst made according to the present invention, two such solid superacid catalysts designated A and B were prepared, and their compositions and BET surface areas were characterized as shown in *Table 1*.

Table 1

	Unsupported Catalyst A	Supported Catalyst B
Catalyst composition	Ni/ZrO ₂ /SO ₄	Ni/ZrO ₂ /SO ₄ /Al ₂ O ₃
Catalyst analysis, wt. %		
Ni	2.0	2.0
ZrO ₂	93.9	11.2
SO ₄	4.1	6.4
*Al ₂ O ₃	0	80.4
BET surface area, m ² /g	101	158

* BET surface area of Al₂O₃ support material is 186 m²/g; particle size was 60 mesh (U.S. Sieve Series) or 0.250 mm.

As shown in *Table 1*, the supported catalyst B contains about 80 wt. % support material while the total active material specified as Ni/ZrO₂/SO₄ is only about 20 wt%. Due to precipitation of the active metals onto the high surface area support material Al₂O₃, the surface area of supported catalyst B was increased by about 60%.

The catalytic activities of these two solid superacid catalysts A and B towards cracking of plastics and alkylation of aromatics were compared using the same reaction conditions. A 20 ml microautoclave was successfully charged with 1.0 gram of dry catalyst and 1.0 gram of polypropylene having average molecular weight of 250, 000. Four grams of toluene were added as the aromatic solvent compound. The catalytic reaction conditions used and conversion of the plastics feed to toluene soluble products for operations with each catalyst A and B are provided in *Table 2*. Product structures were identified by gas chromatography-mass spectrography (GC-MS) and conversion levels achieved were further quantified by gas chromatography.

TABLE 2

		Unsupported Catalyst A	Supported Catalyst B
Reaction Conditions			
5	Temperature, °C	425	425 ^a
	Pressure, psig	0	0
	Time, min	30	30
Product Analysis			
10	Conversion to toluene solubles, wt%	100	100
	^a Catalyst activity, g.product/g.active material.hr	2.0	10.0
	^b Selectivity to alkylated aromatics, wt. %	90	90

(a) Catalyst active material is defined as Ni/ZrO₂/SO₄.

(b) Alkyl groups on alkylated aromatics are C₁-C₄ paraffinic substituents.

As shown in **Table 2**, a complete conversion of polypropylene to toluene solubles is achieved with each catalyst A and B. However, it is seen that the results for supported catalyst B containing about 80 wt% of high surface area alumina support material but having only about 11 wt% of zirconia provided catalytic activity five times greater than that for the known unsupported catalyst A having lower surface area. The liquid products obtained with both catalysts consisted of alkylated aromatics with multibranched alkyl groups (C₁-C₄ paraffinic substituents) attached. Considering that alkylation of aromatics is an acid-catalyzed reaction, it appears that the number of acid sites on catalyst B are substantially greater than on catalyst A. It also appears that in a single reactor with the solid superacid catalyst B, cracking of polypropylene and alkylation of aromatics can occur simultaneously.

EXAMPLE 2

To determine the effectiveness of these same two compositions of solid superacid catalysts in conversion of a waste plastics feed to form alkylated aromatic products, catalysts A and B described in **Table 1** were each introduced successively into a 20 ml microautoclave reactor together with a feed mixture including 0.5 gram polypropylene, 0.5 gram high density polyethylene (HDPE), and 4.0 gram toluene to provide a plastics : solvent weight ratio of 1:4. It is known that HDPE is a major component of typical waste plastics stream and which is the most difficult to crack. The reaction conditions used and results achieved for each solid superacid catalyst are provided in **Table 3**.

TABLE 3

		Unsupported Catalyst A	Supported Catalyst B
Reaction Conditions			
5	Temperature, °C	425	425
	Pressure, psig	0	0
	Time, min	30	30
Product Analysis			
10	Total conversion of plastics, wt%	100	100
	yield of toluene solubles, wt%	76	75
	yield of waxes, wt%	24	
	Catalyst activity, g.product/g.active material.hr	2.0	25
	*Selectivity to alkylated aromatics, wt%	86	10.0
			84

(a) Alkyl groups on alkylated aromatics are C₁-C₄ paraffinic substituents.

- 15 Again, as shown in **Table 3**, complete conversion of the plastics feed material is achieved with each catalyst A and B, and yields of toluene soluble products for each catalyst are about the same. But the catalytic activity of supported catalyst B, defined as weight of product produced from one gram of active material in one hour, is five times greater than that for catalyst A. Thus, the results shown in both **Tables 2** and **3** clearly demonstrate
- 20 that the precipitation of only small concentrations of active solid superacid compounds onto a high surface area support material results in substantial enhancement in catalytic activity for cracking and alkylation of plastics with aromatics solvent feed materials. In this regard, the thermal conversion of such feed materials at 425°C temperature and 1000 psig in hydrogen is only between 15-20 wt. percent.

25

EXAMPLE 3

- A comparison was made between the cracking activity of the supported solid superacid catalyst B with USY-zeolite, known to be a commercial cracking catalyst designated as catalyst C. The feed composition and reaction conditions used for the comparison runs were the same as described in **Table 3**. For comparison, results obtained with catalyst B
- 30 after regeneration, designated catalyst D, was also included as shown in **Table 4**.

TABLE 4

Reaction Conditions		Supported Catalyst B	USY-Zeolite Catalyst C	Supported Catalyst D ^a
5	Temperature, °C	425	425	425
	Pressure, psig	0	0	0
	Time, min	30	30	30
Product Analysis				
10	Total conversion of plastics, wt%	100	100	100
	yield to toluene solubles, wt%	75	51	83
	yield to waxes, wt%	25		17
	Catalytic activity, g.product/g.active material.hr	10.0	49	
	*Selectivity to alkylated aromatics, wt%	84	2.0 A68	10.0 41

a: Catalyst D had the same composition as supported catalyst B, but was regenerated by heating it in air at 550°C for 2 hours to remove carbon deposits

15 b: Alkyl groups on alkylated aromatics are C₁-C₄ paraffinic substituents.

The results of this comparison show that both the supported solid superacid catalyst B and regenerated catalyst D exhibit higher activity than the commercial USY-zeolite catalyst C for conversion of plastics and alkylation of aromatics to toluene soluble products. The catalytic activity of the supported solid superacid catalyst B can be successfully regenerated by heating it in air at 550°C for 2 hours. The lower alkylation selectivity achieved with regenerated catalyst D is believed due to losing some sulfate groups during the high temperature regeneration procedure.

EXAMPLE 4

25 Experimental runs were made in a continuous fixed-bed reactor having 20 ml volume to compare use of a different known unsupported type solid superacid catalyst E and a similar supported catalyst F having an alumina (Al₂O₃) support for alkylation of refinery gases to produce gasoline product. These two catalysts E and F each contained platinum active metal instead of nickel as previously, and had compositions as described in *Table 5*. A

30 typical refinery gas designated feed F1 was reacted with the known solid superacid catalyst E and also with new supported solid superacid catalyst F. The refinery gas compositions, the reaction conditions used and results achieved are summarized in *Table 5*.

TABLE 5

Refinery gas composition, vol%:

Feed F-1:			Feed F-2:		
5	Ethylene	30	Propylene	30	
	Propane	20	Isobutane	40	
	Propylene	20	Isobutylene	30	
	Isobutane	10			
	Isobutylene	10			
10	Nitrogen	10			

		Unsupported Catalyst E	Supported Catalyst F	Supported Catalyst G
Catalyst Composition		Pt/ZrO ₂ /SO ₄	Pt/ZrO ₂ /SO ₄ /Al ₂ O ₃	Pt/ZrO ₂ /SO ₄ /Al ₂ O ₃
Catalyst Analysis, wt%				
	Pt	0.5	0.5	0.5
	ZrO ₂	95.3	11.6	15.2
15	SO ₄ ²⁻	4.2	6.5	4.2
	Support (Al ₂ O ₃ or SiO ₂)	0	81.4	80.1
	BET surface area, m ² /g	101	158	196
Reaction Conditions				
	Temperature, °C	150	150	170
20	Pressure, psig	5.0	5.0	5.0
	Gas Hourly Space Velocity, h ⁻¹	200	200	240
	Total Run Time, hr	2 4	24	24
Product Analysis				
			<u>F1</u>	<u>F2</u>
25	Refiner Gas Feed			
	Gasoline formation rate, g/g.active material.hr	0.02	0.12 0.38	0.40
Product distribution				
	iso-C ₅ -C ₁₀	90	98	95
30	iso-C ₁₁ -C ₁₄	10	2	5

Note: Initial BET surface area of Al₂O₃ and SiO₂ were 186 and 345 m²/g respectively.

As shown in **Table 5**, for the supported catalyst F, the gasoline formation rate calculated on the basis of weight of gasoline produced per gram of active material per hour is almost six times greater than that of unsupported catalyst E. Furthermore, the selectivity for undesired higher molecular weight products (C₁₁-C₁₄) was reduced with the supported catalyst F, thereby indicating that further oligomerization reaction was suppressed when the supported solid superacid was used.

Another supported solid superacid catalyst G was prepared by precipitating Pt/ZrO₂/SO₄ onto high surface area silica (SiO₂) support, as described in the catalyst preparation

method. As also shown in *Table 5*, the final BET surface area of silica supported solid superacid catalyst G is increased to 196 m²/g. The activity of the supported solid superacid catalyst G was compared with supported solid superacid catalyst F for alkylation of refinery gases. In the comparison experiments, a refinery gas feed composition F2
5 having composition which resembles that in commercial alkylation processes was used. As shown in *Table 5*, gasoline formation rate of 0.4 g/g active material was achieved with the silica supported solid superacid catalyst G, which was even higher than with alumina supported solid superacid catalyst F. It is believed that supported solid superacid catalyst G has greater active sites than supported solid superacid catalyst F because of its higher
10 surface area.

A correlation between the BET surface area and activity ration for a known unsupported zirconia based solid superacid catalyst and a comparable solid superacid catalysts of this invention is clearly shown by *Figure 1*. The relative activity is expressed as a ratio of catalytic activity for alkylate formation to that of the unsupported solid superacid surface
15 area of the supported catalyst activity ration for alkylation of refinery gas feedstreams is increased much more than proportionately with the available catalytic surface area. This indicates a strong interaction between the active catalytic material (zirconia-based superacid) and the high surface area support material.

A further comparison is made between the long term performance of a supported solid superacid catalyst of this invention and an unsupported solid superacid, as generally shown
20 in *Figure 2*. Curve A shows percent n-butane conversion vs. onstream time for the unsupported solid superacid Mn-Fe/ZrO₂/SO₄ for isomerization of n-butane. Data obtained from "Coal Liquefaction and Gas Conversion", Proceedings of DOE Contractors Review Conference, Pittsburgh, 1995, pp.295, *Figure 4*. Curve B shows alkylation of refinery gas
25 feeds F1 and F2 with supported catalyst Pt/ZrO₂/SO₄/Al₂O₃ conducted at 170°C temperature, ambient pressure, and at 240 gas hourly space velocity. It is seen that the supported solid superacid catalyst remained very active after 72 hours on stream operation.

Although the catalytic activity and effectiveness of the supported solid superacid catalysts according to this invention has been demonstrated on certain feedstocks as described
30 above, these supported solid superacid catalysts are also believed to be useful for catalytic reactions with other feedstocks and processes including hydrocracking and isomerization. Also, although this catalyst invention has been disclosed broadly and in terms of preferred compositions and embodiments, it will be understood that modification and variations can be made within its scope which is defined by the following claims.

WHAT IS CLAIMED IS:

- 1 1. A particulate supported solid type superacid catalyst, comprising:
2 a high surface area support material including alumina (Al_2O_3), silica (SiO_2)
3 or mixtures thereof, said support material having particle size of 0.15-0.84 mm (0.006-
4 0.033 inch) and original surface area of 100-500 m^2/gm .; a transition metal oxide or
5 oxyhydride of a Group IV metal including hafnium (Hf), titanium (Ti), zirconium (Zr), or
6 mixtures thereof which is precipitated onto said support material, said transition metal oxide
7 or oxyhydride being anion modified by addition of molybdate (MoO_4), phosphate (PO_4),
8 selenate (SeO_4), sulfate (SO_4) or tungstate (WO_4); said transition metal oxide or oxyhydride
9 being further stabilized against deactivation by addition of an active promotor metal for
10 providing a hydrogenation function, said active promotor metal being a base metal including
11 cobalt (Co), nickel (Ni) or palladium (Pd), or a noble metal including platinum (Pt), rhodium
12 (Rh), or ruthenium (Ru), or mixtures thereof, all provided uniformly on said support material,
13 said transition metal oxide or oxyhydride being 5-20 wt % of the total catalyst and said
14 active promotor metal being 0.05-5 wt.% of the total catalyst, so as to provide a supported
15 solid superacid catalyst which is non-corrosive and has a final total surface area of 100-450
16 m^2/gm .
- 1 2. A supported solid superacid catalyst according to *claim 1*, wherein said support
2 material has particle size of 30-60 mesh (U.S. Sieve Series) (0.60-0.25mm) and initial
3 surface area within the range of 140-450 m^2/gm ., said support material being 70-90 wt.
4 % of the total catalyst.
- 1 3. A supported solid superacid catalyst according to *claim 1*, wherein said transition
2 metal oxide is aqueous precipitated onto said support material in a substantially uniform
3 layer and provides 6-18 wt%. of the total catalyst.
- 1 4. A supported solid superacid catalyst according to *claim 1*, wherein said anion
2 modification compound is 2-8 wt.% of the total catalyst.
- 1 5. A supported solid superacid catalyst according to *claim 1*, wherein said active
2 promotor metal is cobalt (Co), nickel (Ni), palladium (Pd), or platinum (Pt), and mixtures
3 thereof, and is 0.1-4 wt.% of the total catalyst.
- 1 6. A solid superacid catalyst according to *claim 1*, wherein based on the total catalyst
2 said support material is 70-90 wt. %, said active transitional metal oxide coating is 6-18
3 wt. %, said anion modification material is 4-7 wt.%, and said additive stabilizing metal is
4 0.1-4 wt. % of the total catalyst.

1 7. A solid superacid catalyst material according to *claim 1*, wherein the total pore
2 volume is 0.1-0.5 cc/gm and the final surface area after a calcination step is 130-400
3 m²/gm.

1 8. A particulate supported solid type catalyst, comprising:
2 a high surface area support material including alumina (Al₂O₃), silica (SiO₂)
3 or mixtures thereof, said support material having particle size of 0.15-0.84 mm (0.006-
4 0.033 inch) and original surface area of 140-450 m²/gm;
5 a transition metal oxide or oxyhydride of a Group IV metal including hafnia
6 (HfO₂), stannic oxide (SnO₂), titania (TiO₂), or zirconia (ZrO₄) or mixtures thereof which is
7 aqueous precipitated onto said support material, said transition metal oxide or oxyhydride
8 being anion modified by addition of molybdate (MoO₄), phosphate (PO₄), sulfate (SO₄) or
9 tungstate (WO₄);
10 said transition metal oxide or oxyhydride being further stabilized by addition
11 of an active promotor metal providing a hydrogenation function, said active promotor being
12 a base metal including cobalt (Co), nickel (Ni) or palladium (Pd), or a noble metal including
13 platinum (Pt), or mixtures thereof all provided uniformly onto said support material, said
14 support material being 70-90 wt.% of the total catalyst, said transition metal oxide or
15 oxyhydride being 6-18 wt.% of the total catalyst, and said active promotor metal being
16 0.1-4 wt.% of the total catalyst, so as to provide a supported solid superacid catalyst
17 which is non-corrosive and has a final total surface area of 100-400 m²/gm.

1 9. A method for producing a supported solid superacid catalyst material, comprising
2 the steps of:
3 (a) providing a support material having an initial surface area of 100-500
4 m²/gm, said support material including oxides of aluminum, silicon, or mixtures thereof;
5 (b) precipitating hydroxides of Group IV metals selected from the group
6 consisting of hafnium (Hf), tin (Sn), titanium (Ti) and zirconium (Zi) or mixtures thereof onto
7 said support material;
8 (c) modification treating said support material and said metal hydroxides
9 with an anion compound including molybdate (MoO₄), phosphate (PO₄), sulfate (SO₄) or
10 tungstate (WO₄);
11 (d) adding an active promotor metal selected from the group consisting of
12 cobalt (Co), nickel (Ni), iridium (Ir), Osmium (Os), palladium (Pd), platinum (Pt), rhodium (Rh)
13 and ruthenium (Ru) to said modified support material; and
14 (e) calcining said support material together with said precipitated metal
15 compounds at 500-650°C temperature for 2-4 hours to produce the supported solid
16 superacid catalyst having final high surface area of 100-450 m²/g.

1 10. The method of claim 9, including precipitating said metal hydroxides onto said metal
2 oxide support material by aqueous precipitation.

1 11. A catalytic reaction process for alkylation of refinery gases feed to produce a high
2 octane gasoline product, the process comprising reacting a refinery gas feedstock with a
3 supported solid superacid catalyst as defined by *claim 1* under reaction conditions of 70-
4 250°C temperature, 0-500 psig. pressure, and 100-1000 Vf/hr/Vc space velocity and
5 withdrawing a high octane gasoline product.

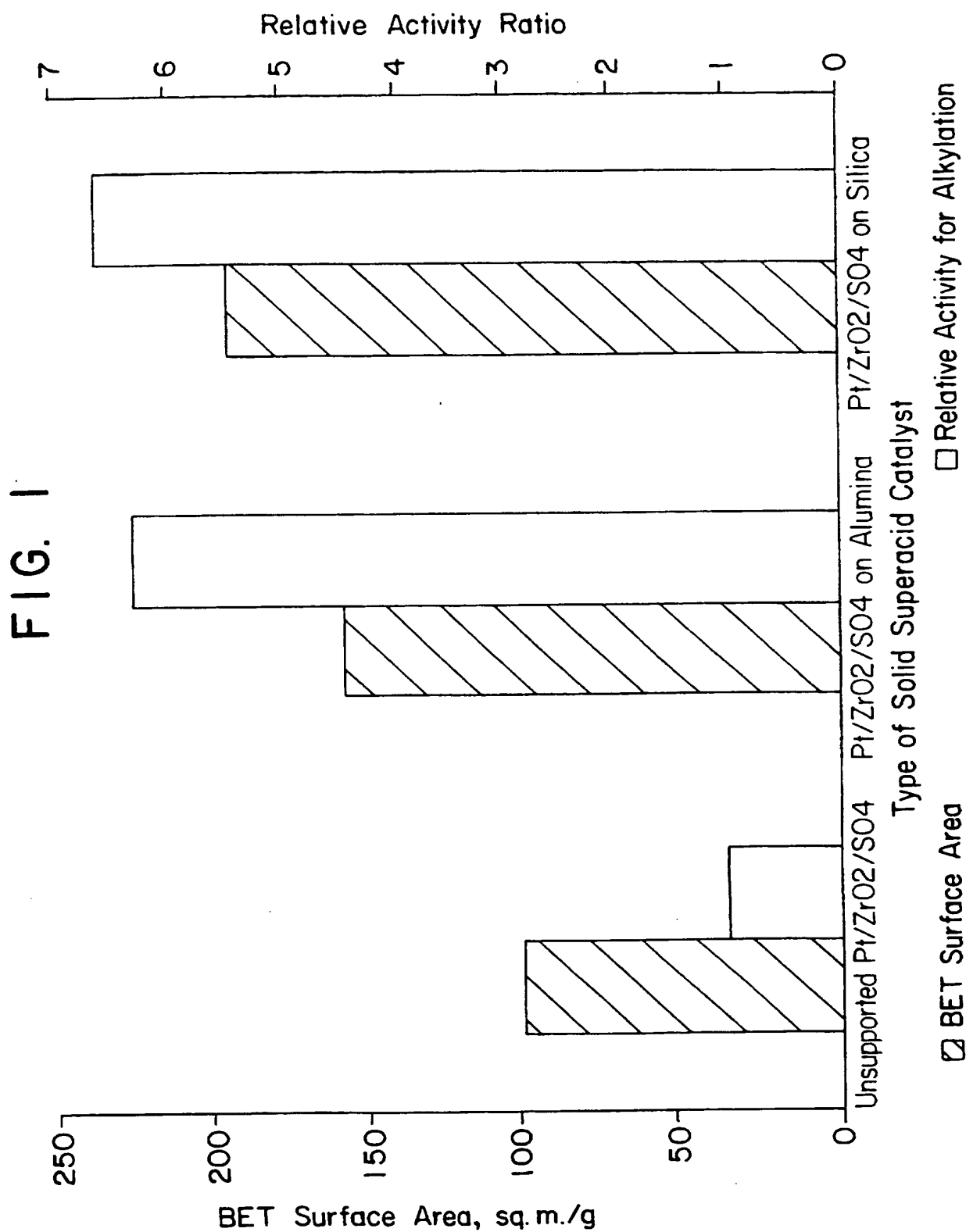
1 12. A catalytic reaction process according the *claim 11*, wherein the reaction conditions
2 are 100-200°C temperature, 0-200 psig. pressure, and 160-400 Vf/hr/Vc space velocity.

1 13. A catalytic reaction process for hydrocracking a polyslefinic feed material including
2 high density polyethylene and polypropylene and simultaneously alkylating an aromatic
3 compound feedstock in a single reactor, the process comprising reacting the feedstock with
4 a supported solid superacid catalyst as defined by *claim 1* under mild reaction conditions
5 of 100-500°C temperature and 0-100 psig. pressure and producing aromatic products.

1 14. A catalytic reaction process according to *claim 13*, wherein the reaction conditions
2 are 125-450°C temperature and 10-80 psig. pressure.

1 15. A method for regenerating a supported solid superacid catalyst, including the steps
2 of contacting the used catalyst with air at 500-650°C temperature for 2-4 hours.

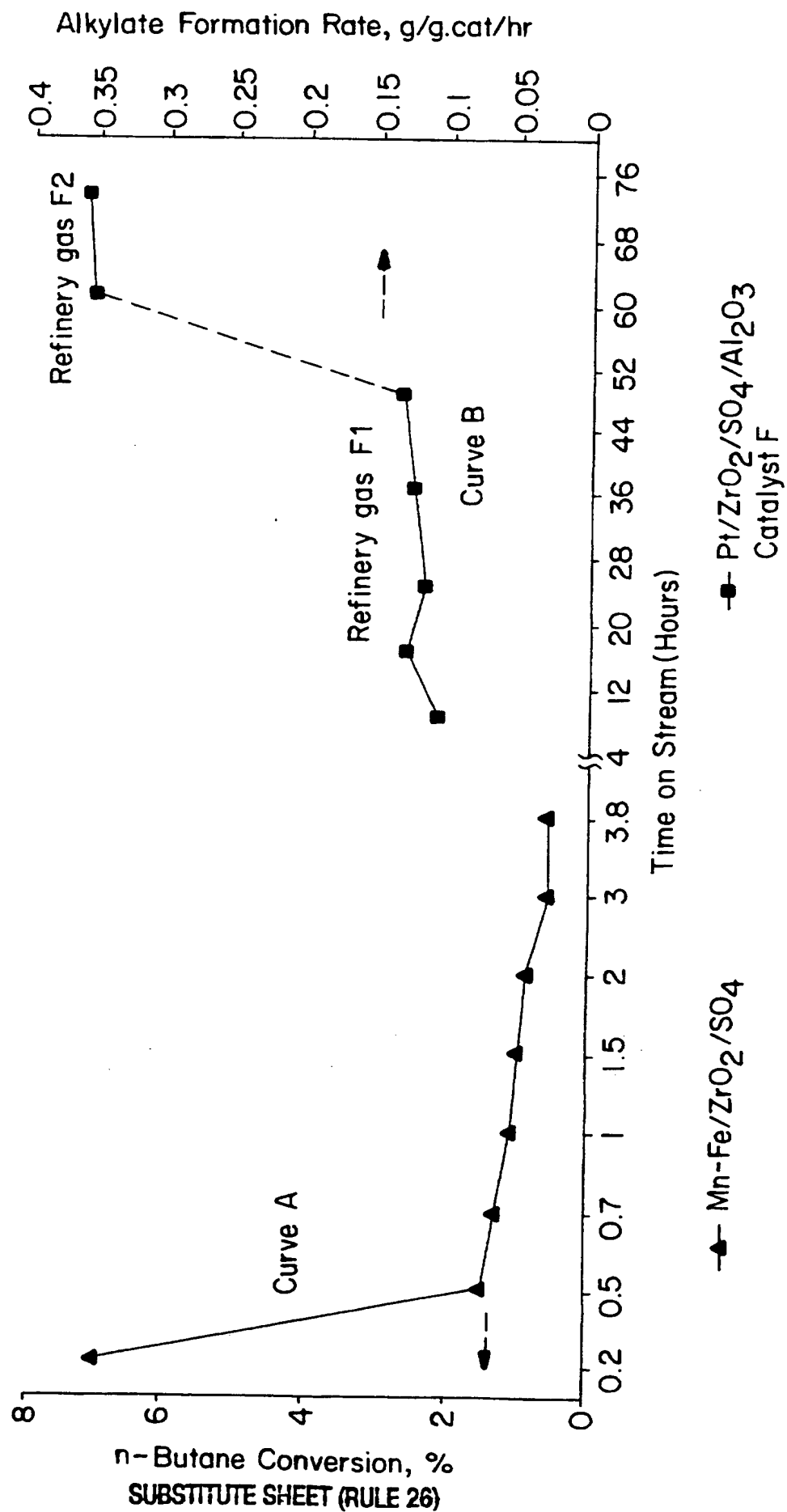
1 / 2



SUBSTITUTE SHEET (RULE 26)

2 / 2

FIG. 2



INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/US 96/18436

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01J27/053 B01J27/057 B01J27/14 C07C2/58 C07C4/06
C10G45/62

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01J C07C C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 527 031 A (EXXON RESEARCH ENGINEERING CO) 10 February 1993 see page 2, line 20 - page 3, line 10 ---	1-6,8-10
A	EP 0 624 637 A (ENIRICERCH SPA ;AGIP PETROLI (IT)) 17 November 1994 see claims 1-14; examples 1,2,7-9; table 1 ---	1-6,8-14
A	EP 0 174 836 A (RES ASS UTIL LIGHT OIL) 19 March 1986 see page 2, line 12 - page 7, line 10; examples 6-11; tables 1,3,4 ---	1,3-6, 8-14
A	US 5 382 731 A (CHANG CLARENCE D ET AL) 17 January 1995 see the whole document ---	1,4-6, 8-14
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
- * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

- * "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- * "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- * "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * "&" document member of the same patent family

Date of the actual completion of the international search

6 March 1997

Date of mailing of the international search report

19. 03. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 PatentAan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Cubas Alcaraz, J

INTERNATIONAL SEARCH REPORT

Internat: I Application No
PCT/US 96/18436

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 666 109 A (SUN CO INC R & M) 9 August 1995 see claims 1-30 ---	1-6,8-14
A	EP 0 605 279 A (INST FRANCAIS DU PETROL) 6 July 1994 see the whole document ---	1,2,7-9
A	EP 0 542 612 A (INST FRANCAIS DU PETROL) 19 May 1993 see the whole document ---	1-14
A	EP 0 653 398 A (SUN CO INC R & M) 17 May 1995 cited in the application see the whole document -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat Application No

PCT/US 96/18436

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0527031 A	10-02-93	US 5113034 A	12-05-92
		CA 2073473 A	06-02-93
		JP 5213781 A	24-08-93

EP 0624637 A	17-11-94	JP 7051572 A	28-02-95
		US 5518978 A	21-05-96

EP 0174836 A	19-03-86	JP 1859016 C	27-07-94
		JP 61220738 A	01-10-86
		JP 1816745 C	18-01-94
		JP 5029503 B	30-04-93
		JP 61068137 A	08-04-86
		JP 1816746 C	18-01-94
		JP 5029505 B	30-04-93
		JP 61068138 A	08-04-86
		JP 1816749 C	18-01-94
		JP 5029504 B	30-04-93
		JP 61153140 A	11-07-86
		JP 1816750 C	18-01-94
		JP 5029506 B	30-04-93
		JP 61153141 A	11-07-86
		DE 3586228 A	23-07-92
		US 5036035 A	30-07-91
		US 5120898 A	09-06-92

US 5382731 A	17-01-95	AU 7367094 A	20-02-95
		CA 2169637 A	02-02-95
		EP 0710221 A	08-05-96
		WO 9503262 A	02-02-95

EP 0666109 A	09-08-95	US 5516964 A	14-05-96
		US 5494571 A	27-02-96
		US 5494569 A	27-02-96
		CA 2140700 A	22-07-95
		JP 7265705 A	17-10-95

EP 0605279 A	06-07-94	FR 2699429 A	24-06-94
		JP 6277523 A	04-10-94

EP 0542612 A	19-05-93	FR 2683740 A	21-05-93

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US 96/18436

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0653398 A	17-05-95	US 5493067 A	20-02-96
		CA 2135269 A	13-05-95
		JP 7238040 A	12-09-95
